Use and Misuse of Chemical Reactivity Spreadsheets

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INTRODUCTION

Misidentifying chemical hazards can have deleterious effects. Consequences of not identifying a chemical are obvious and include fires, explosions, injury to workers, etc. Consequences of identifying hazards that are really not present can be equally as bad. Misidentifying hazards can result in increased work with loss of productivity, increased expenses, utilization/consumption of scarce resources, and the potential to modify the work to include chemicals or processes that are actually more hazardous than those originally proposed. For these reasons, accurate hazard identification is critical to any safety program.

Hazard identification in the world of chemistry is, at best, a daunting task. This task can be difficult because one cannot know or understand which reactions may be hazardous between the approximately twelve million known chemicals. Other variables, such as adding other reactants/contaminants or changing conditions (e.g., temperature, pressure, or concentration), make hazard determination something many would construe as being more than impossibly difficult. Despite these complexities, people who do not have an extensive background in the chemical sciences can be called upon to perform chemical hazard identification. Because hazard identification in the area of chemical safety is so burdensome and because people with a wide variety of training are called upon to perform this work, tools are required to aid in chemical hazard identification. Many tools have been developed. Unfortunately, many of these tools are not seen as the limited resource that they are and are used inappropriately.

MSDS LIMITATIONS

The most common of these tools is the Material Safety Data Sheet (MSDS). MSDS are valuable tools to use in the hazard identification process, but these MSDS have their limitations.

- One limitation is that MSDS tend to be vague when it comes to chemical reactivities. Specific reactions or reaction conditions are often not provided. For example, some MSDS for acetic acid indicate that acetic acid is incompatible with ammonium salts, but this does not provide sufficient information to determine potential reactivities and conditions necessary to result in a dangerous reaction. A mixture of ammonium nitrate and acetic acid will react upon heating and adding ammonium thiosulfate to acetic acid will cause the release of sulfur dioxide (1), but no reaction will occur when acetic acid is mixed with ammonium chloride or many other ammonium salts. How can one determine which ammonium salts are dangerous to mix with acetic acid from vague statements like those presented on some MSDS?

- Incompatibilities listed in MSDS typically do not indicate whether the incompatibility is a quality or safety issue or what should be expected if the incompatible mixing of two components should occur (e.g., pressurization, toxic gas release, heat, fire, explosion).
- Another limitation of MSDS is that they frequently use jargon that makes it difficult for some people to understand. Terms such as alkali metals, alkali earths, reactive metals, halogens, oxidizers, etc., can leave those who are not well versed in chemistry confused. What can cause this to become more confusing is that some chemical properties can be dependent more upon the conditions than the chemical (e.g., sulfuric acid is sometimes listed as an oxidizer and will display oxidizing capabilities only under certain conditions.) Because of these difficulties, the use of MSDS to determine chemical reactivities does not always provide the desired information.

Other sources that people use to determine chemical reactivities are reference materials such as books and Web sites. These reference materials tend to provide more in-depth information, but have drawbacks of their own. Web sites can be difficult to find, navigate within, and typically contain only MSDS-type information. Books can be expensive and not always available. Also, these references don't always agree with each other and vary in the amount of information provided. Some books such as Sax's *Dangerous Properties of Industrial Materials* (2) provide information similar to that found in MSDS and others such as *Bretherick's Handbook of Reactive Chemical Hazards* (3) provide much more in-depth information. Lastly, there is no definitive reference that can easily be understood by all. Because of these issues, the use of reference materials tends to be limited to the more easily understood and widely used publications such as Sax's (2).

CHEMICAL REACTIVITY WORKSHEETS

Numerous chemical reactivity worksheets have been developed in an effort to overcome the above listed shortcomings of various data resources and to simplify chemical reactivity hazard identification. Chemical reactivity worksheets are available on the Internet and are designed for easy use. While they provide good information, they are, many times, misused or misapplied. It is important to understand the intent of these worksheets, their limitations, and how they can be properly used if they are to be incorporated into a chemical hazard identification process.

Short, Consolidated Spreadsheets

Short, consolidated spreadsheets have the advantage of providing much information in a small format. A typical example of these types of spreadsheet would be the one originally developed by the US Environmental Protection Agency which is available at numerous university web sites. (4-9)

This specific spreadsheet identifies chemicals as being in one or more of 41 different chemical hazard classes and then provides information on how one hazard class of chemical could react with another class. Spreadsheets like this can be used as powerful tools and can provide good initial information that can help identify potential chemical reactivity hazards. Unless one understands chemistry and the limitations of these spreadsheets, one can "identify" hazards that do not exist or miss hazards that do exist.

If one uses the EPA spreadsheet as an example, then one can see some of the limitations posed by short, consolidated, chemical reactivity spreadsheets.

1. Chemical Class Determination. The first difficulty encountered in using these spreadsheets is determining what chemical class should be used for the product in question. Since membership to a class is typically based upon functional groups present, any chemical having more than one functional group can be a member of more than one chemical class. For example, nitrobenzene would be classified both as an organic nitro compound and as an aromatic hydrocarbon. To use this spreadsheet correctly, one must consider reactivities of both reactivity groups. Other reactivity groups are based upon chemical properties. Classifying a chemical into these groups can be difficult when a chemical's property is dependent upon conditions. An example for this situation is sulfuric acid. Typically, sulfuric acid will be characterized as being a mineral acid, but, under some conditions, it will behave as an oxidizing acid which would make it a member of a different reactivity group. (See Figure 1.) Another example of a condition that could affect the placement of a chemical into a specific reactivity classification is concentration. Concentrated sulfuric acid would be classified as being both water reactive and corrosive reactive but, if the acid is sufficiently diluted, one or both hazard classifications are no longer valid.

EPA-600/2-80-076 April 1980
A METHOD FOR DETERMINING THE COMPATIBILITY OF CHEMICAL MIXTURES

No.	Reactivity Group Name		
1	Acids, Mineral, Non-oxidizing	1	
2	Acids, Mineral, Oxidizing		2
106	Water and Mixtures Containing Water	H	H

Legend

Code	Consequences
H	Heat Generation

Figure 1. EPA spreadsheet example. Is sulfuric acid a mineral acid or an oxidizing acid?

2. Chemical Class Identification. Chemical reactivity classes can be confusing due to vague descriptions. When one observes the hazard classification of "Explosive", one does not know whether picric acid should be included in that group or not. Also, one must be well versed on chemical nomenclature to ensure the correct chemical class definition is applied. Everybody should know that acetonitrile should be classed as a

"Nitrile", but less well informed personnel may become confused when they see a synonym of acetonitrile as methyl cyanide and try to classify this product as a "Cyanide."

3. Chemical Class Definition. When spreadsheets such as these are constructed, efforts are made to determine when chemicals from one class will react unfavorably with another class. If one example can be found, then the entire class is listed as being incompatible with the other class. If the user of the spreadsheet does not realize this, then one can identify "hazards" that do not exist. For example, potassium cyanide does not behave similarly to potassium ferricyanide. Likewise, "Water Reactive" products are stated to be incompatible with everything, including other water reactive materials. If this is the case, then how can "Water Reactive" chemicals be stored, since they would be incompatible with the storage container? How could alkali metals be stored under kerosene? The list of examples could go on endlessly.

4. Chemical Class Omissions. Not all chemical classes are present on many spreadsheets which can lead to hazards not being identified. A common omission is the category of "Air." Air may be considered to be a member of the "Oxidizer" hazard group in some tables, but this is usually not explained well and, if it is considered to be in the "Oxidizer" group, then the culprit will be the oxygen present. In this case, reactions such as the one between lithium and nitrogen will not be identified.

5. Limited to Binary Mixtures. Short spreadsheets may not address reactions involving multiple reactants. This creates a number of potential issues. If, for example, a hazardous reaction requires an acid to be present as a catalyst, then the spreadsheet may not list the two non-acid components as being incompatible which could lead to a false sense of security. If the spreadsheet assumes the acid to be present and the two non-acid components are listed as being incompatible, then hazards would be identified where none would exist if no acid were present. Another difficulty is the potential of sequential reactions and any resulting incompatibility. Calcium carbide may not be listed on the spreadsheet as being hazardous when in the presence of bronze or copper, but the carbide will react with water in the air to form acetylene which will then react with the bronze or copper to form explosive copper acetylide.

6. Vague, Misleading, or Incorrect Reaction Descriptions. Because these spreadsheets are short, descriptions of hazardous reactions are typically vague. These vague descriptions may be misleading or even incorrect. Mixtures of acetic and nitric acid are described in short spreadsheets to result in heat and gas generation, yet these mixtures have been reported to explode (3). Caustics and cyanides are listed as having no reaction even though the presence of alkali favors explosive polymerization (3).

7. Unknown Pedigree/Disclaimers. Some spreadsheets are taken from sources more than once removed from the original source. Two primary issues result from this practice. The first is that any disclaimer or applicability statement that may have been present in the original publication may not have survived being transplanted. For example, a spreadsheet published in *Safety in Academic Chemistry Laboratories* (10) has been found to be recreated in numerous sources, such as chemical hygiene plans and other

documents. What is missing is that this table applies to academic laboratories but it is being used in non-academic environments. Also, the disclaimer in the original indicating that this spreadsheet is a guide and that other sources such as *Bretherick's* (3) should be used for specific information are missing from verbiage describing the spreadsheet in these other documents. (See Figure 2.) A second issue is that the spreadsheet is, many times, not referenced so one cannot go back to the original source for further information. The result is that this spreadsheet appears to be an accurate table when in reality it is a very short sample of incompatible reactions. If one does not know how to question spreadsheets such as this one, one will not know that simple and obvious potentially hazardous reactions such as the one between permanganate and reducing agents such as sodium thiosulfate will occur.

Appendix 2. Incompatible Chemicals

Use this table only as a guide. Specific incompatibilities are listed in MSDSs. Consult *Bretherick's Handbook of Reactive Chemical Hazards* (Urben, P. G.; 6th ed.; Butterworth-Heinemann: London, 2000; book and CD-ROM) for an extensive listing and thorough discussion of chemical incompatibilities.

Chemical	Incompatible with
Nitric acid	Acetic acid, aniline, sulfuric acid, chromic acid, hydrocyanic acid, hydrogen sulfide, flammable/combustible liquids and gases, copper, brass, heavy metals, alkalis
Sulfuric acid	Permanganates, water, aqueous solutions, reducing agents, chlorates, perchlorates, nitric acid

Figure 2. Example of disclaimer that is often missing in publications.

Reactivity Matrices

Some feel that limitations posed by these short spreadsheets pose too many restrictions upon the act of chemical hazard identification so attempts have been made to produce very large matrices that address specific chemical interactions with other specific chemicals. Because these chemical specific matrices can become quite large, they are usually built around a parsing function that allows one to call up chemicals of specific interest. A commonly used chemical reactivity spreadsheet is the one published by the National Oceanographic and Atmospheric Administration (NOAA) (11) (http://response.restoration.noaa.gov/chemaids/react.html). The spreadsheet can be installed on the user's computer and then the user can input those chemicals of interest and a chemical reactivity matrix will be generated. Because these chemical reactivity matrices focus on specific chemicals of interest, they can become very powerful tools. Unfortunately, these matrices are too often blindly used without the user realizing or understanding those limitations present that could provide either incorrect or inappropriate information. Users need to understand that the limitations present in these reactivity matrices are not only the same as those described above but also include the following.

1. Assumptions. The greatest limitation present in reactivity matrices is that one does not know what assumptions have gone into determining how reactivity hazards were identified. In some cases, hazardous reactions identified in reactivity

matrices seem confusing. When one looks up the potential reaction between hydrochloric acid and calcium hydroxide, one finds several curious statements.

The first is that no concentration of the hydrochloric acid is given so one must assume that it is concentrated. Likewise, one must assume that the calcium hydroxide is in the crystalline form.

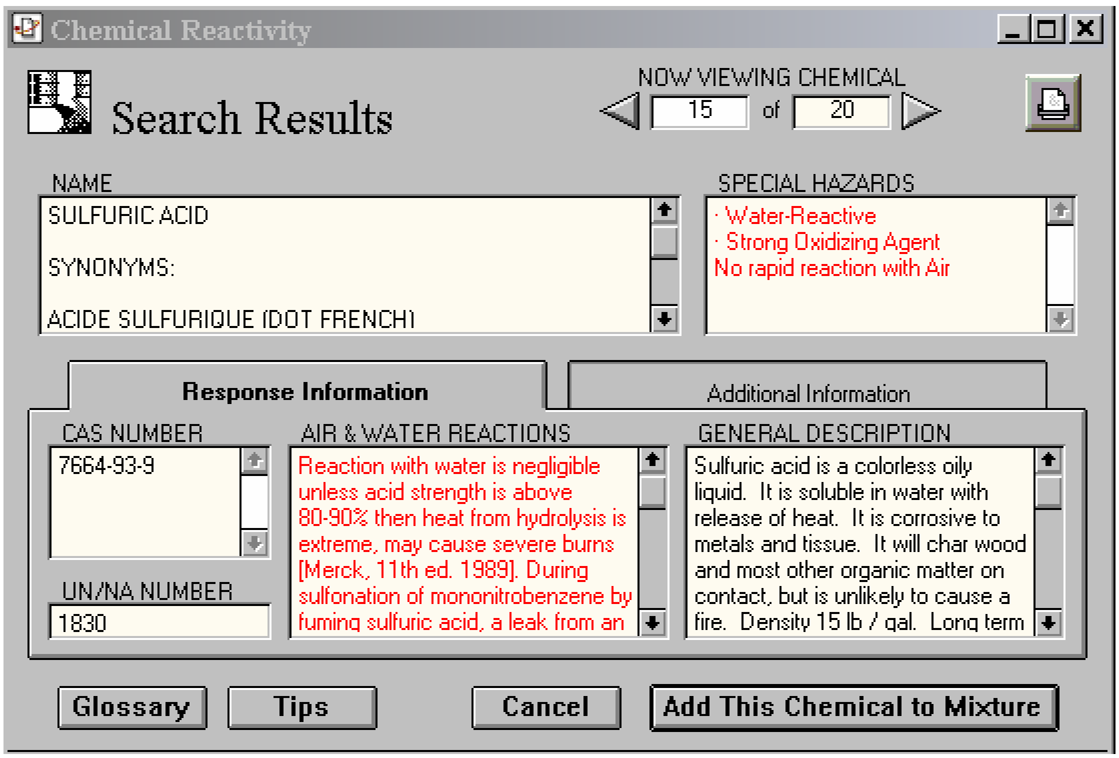
A second is that hydrochloric acid is considered to be air reactive. Typically, statements like “air reactive” indicate that the chemical will react in air to form toxic, flammable, explosive, or some other hazardous product. Since assumptions or conditions are not known here, one does not know if the air reactive statement refers to the simple fuming that one observes as hydrochloric acid off gases. This would not be considered to be “air reactive” in the traditional sense, but off gassing may be part of the “air reactive” definition according to NOAA. The difficulty with information such as this is that one might think that hydrochloric acid will react with air to form another product that has other hazards due to the air reactivity classification.

A third curious statement is that the reactivity matrix indicates that mixing hydrochloric acid with calcium hydroxide could result in a fire. Once again, assumptions made that resulted in this statement being generated are not known. Clearly, the addition of these two chemicals will result in the generation of heat, but the temperature of the mixture should be limited by the boiling point of the aqueous mixture. In an extreme situation where if a person were to add solid calcium hydroxide to a container of hydrochloric acid, one might get a steam pocket formed in the bottom of the container and the rapid ejection of the aqueous mixture. In no circumstances, however, is there anything in the mixture that could ignite. It is unlikely the assumption was being made that this mixture could be generated proximate to a flammable material such as a solvent and that the heat generated could initiate a fire of the solvent. If this assumption was being made, then any reaction that could generate heat would have been listed as having a potential for causing a fire.

2. Hazards Not Identified. Having a chemical reactivity matrix present that shows potential hazardous reactions does not guarantee that all hazardous reactions will be cited. When one mixes sulfuric acid with hydrofluoric acid, the reactivity matrix indicates that only heat will be generated. What is absent from the matrix is that sulfuric acid will bind much of the water present in the hydrofluoric acid and will cause hydrogen fluoride gas to be copiously generated. Hydrogen fluoride is both a corrosive and a highly toxic gas and not identifying this type of hazard could lead to dangerous situations.

3. Binary Mixtures. As with all spreadsheets, a great weakness is their inability to identify hazards associated with mixtures. This problem can arise in several ways. One way this problem can arise is in the hazard evaluation of diluted chemicals. Concentrated sulfuric acid is considered a water reactive material, but sulfuric acid diluted in water is not. If one mixes diluted sulfuric acid with another water-

containing product, then a reaction may not occur even though the spreadsheet indicates that one would. This means that one cannot simply take every constituent present in a mixture and look at potential reactivities in an attempt to determine if an adverse reaction will occur. (See Figure 3.) In this example, the incorrect identification of the consequences of mixing would not lead to any adverse effects, except for the additional time and costs associated with mitigating a non-existent hazard.



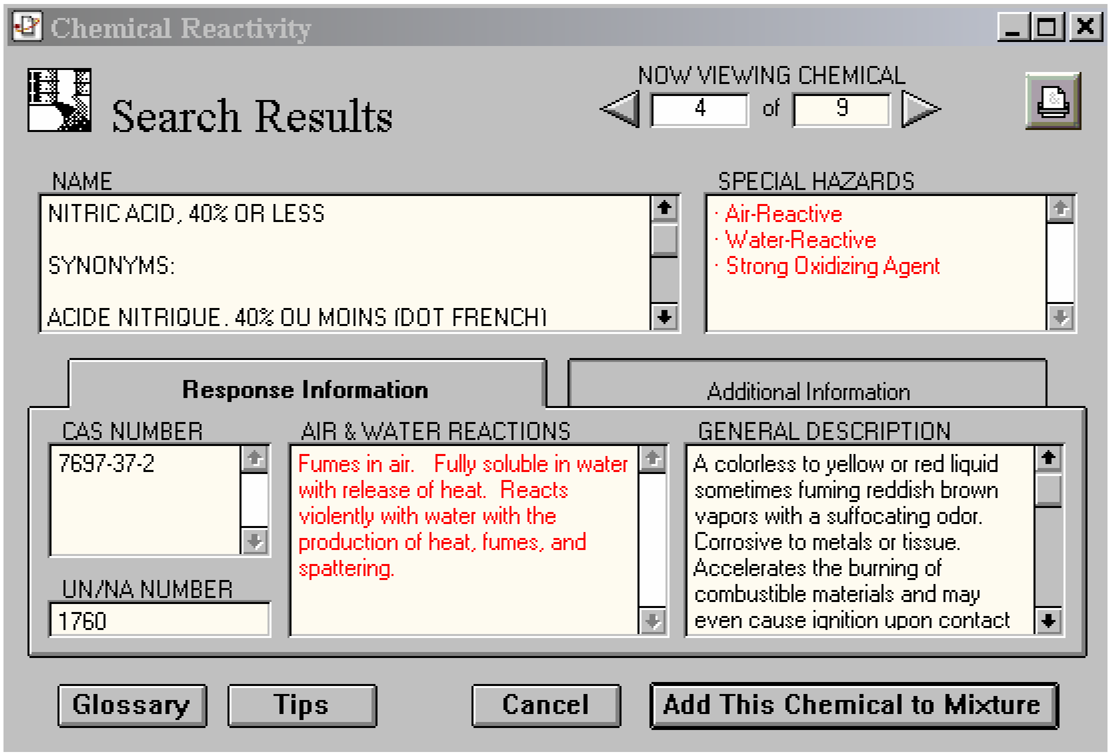


Figure 3. NOAA chart for mixing sulfuric and nitric acid.

4. <u>Three or More Component Interaction</u>. Sulfuric acid + nitric acid + glycerine (See Figure 4.)

Chemical matrices show that the reaction of glycerine with sulfuric acid will result in the generation of heat and gas. These spreadsheets will also indicate that the reaction between glycerine and nitric acid will cause heat and gas generation. According to this information, venting a container of these chemicals will prevent a pressure-volume explosion. What the spreadsheet does not indicate is that mixing glycerine, sulfuric acid, and nitric acid together can generate nitroglycerine which can lead to a very powerful explosion which will not be mitigated by keeping the reaction vessel vented to the atmosphere.

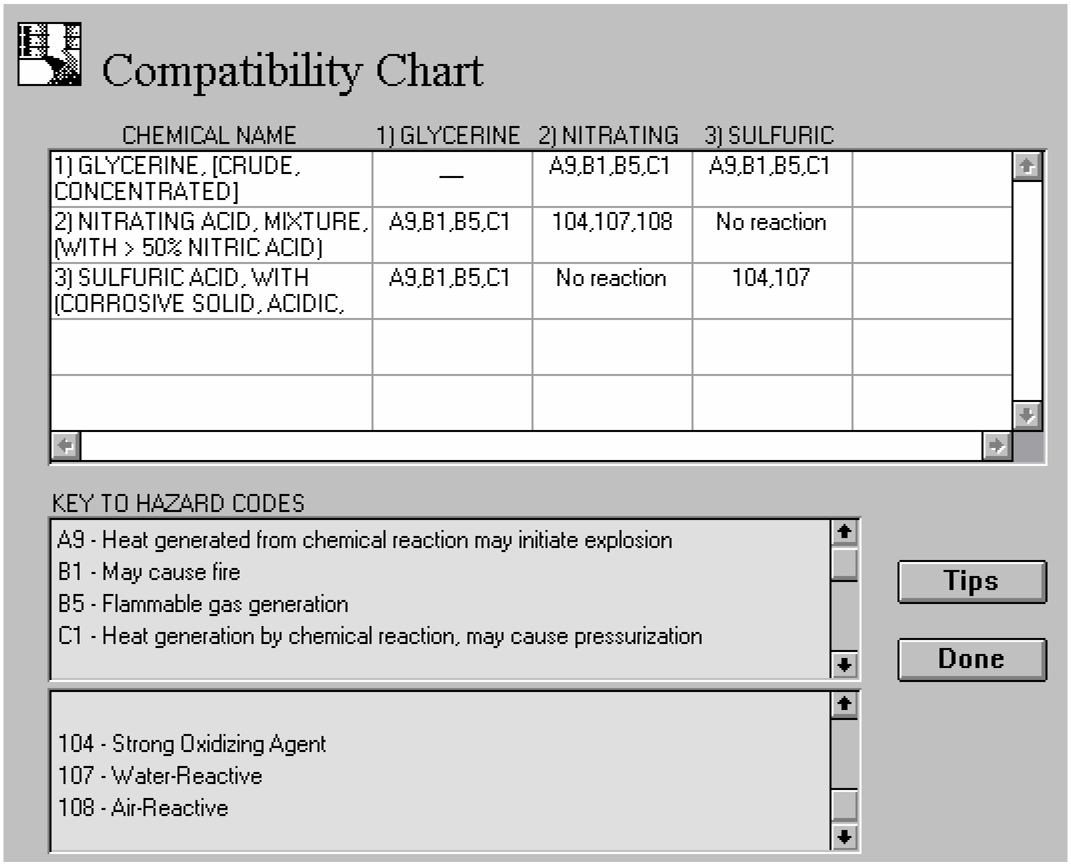


Figure 4. NOAA chart for mixing glycerine, nitric acid, and sulfuric acid.

Proper Use of Chemical Reactivity Matrices

As stated before, chemical hazard identification is a difficult and complex task due to the number of chemicals known and how they will behave differently under different conditions. Because of this enormous complexity, it should come as no surprise that there is no single perfect tool that will perform chemical hazard identification. For those reasons described above, blindly using chemical reactivity matrices as the sole source to determine the potential for adverse chemical reactions is foolish at best and dangerous or deadly at worst.

Chemical reactivity matrices are incredibly powerful tools, but they must be used correctly. To use them correctly is to use them in conjunction with other resources. Chemical reactivity matrices and MSDS are natural places to start when a reactivity hazard determination is being performed. One starts by determining the chemicals that are going to be used, those conditions under which they are to be used, and then those chemicals that might be or are present that could potentially cause a problem using chemical reactivity matrices and MSDS. Other reliable resources, such as *Bretherick's Handbook of Reactive Chemical Hazards* (3) or *NFPA 491, Guide to Hazardous Chemical Reactions* (1), should then be consulted to see if a potentially hazardous reaction exists under the foreseeable conditions of the proscribed work. Lastly, and most importantly, seek the advice of a person who is knowledgeable in chemistry – even if you yourself are knowledgeable in chemistry. This other person can take the information you have and help put it into perspective or can help identify other reactions that may have been overlooked. Most of all, this other person can simply ask the question, "Does this make sense?"

CONCLUSION

We have discussed what we believe to be a representative sample of the hazard identification tools available. While all of the available tools are valuable, they do have limitations and should only be used as part of a comprehensive evaluation process conducted by safety professionals with an in-depth knowledge of chemistry. Misuse and over-reliance on these tools can be costly in terms of personal safety, public safety, environmental safety, and property damage when hazards are not identified and mitigated, or costly, when hazards are misidentified, leading to controls to mitigate hazards that do not exist.

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